



# On the influence of the nucleation overpotential on island growth in electrodeposition

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## ABSTRACT

Electrochemical deposition of a metal onto a foreign substrate usually occurs by an island growth mechanism. A key feature of island growth for a material  $M$  on a foreign substrate  $S$  is that the onset potential for deposition is shifted negative from the equilibrium potential for the metal ion couple. The nucleation overpotential, defined as  $\eta_n(M^+/S) = |U_n(M^+/S) - U_{eq}(M^+/M)|$ , influences key aspects of deposition of a metal on a foreign substrate. Here we discuss how the nucleation overpotential influences the kinetics of island growth, the implications of the nucleation overpotential on island shape and orientation, and the consequences of the coupling between the island density (applied potential) and the island size at coalescence (grain size). We then discuss the kinetics of island growth in terms of the contributions to vertical and lateral growth. Finally, we present examples of experimental methods to manipulate the nucleation overpotential and overcome some of the limitations imposed by the nucleation overpotential.

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## 1. Introduction

For many systems of technological interest, electrochemical deposition of a material onto a foreign substrate occurs by Volmer–Weber island growth. The growth mode is dictated by the interaction energy between the metal adatoms and the substrate ( $E_{M_{ads}-M}$ ), and the interaction energy between the metal adatoms and the native substrate ( $E_{M_{ads}-S}$ ) [1]. Deposition occurs by the Volmer–Weber island growth mechanism when  $E_{M_{ads}-S} < E_{M_{ads}-M}$ . Macroscopically this can be viewed as deposition of a material onto a non-wetting substrate.

A characteristic feature of Volmer–Weber island growth in electrocrystallization is that the onset potential  $U_n(M^+/S)$  for deposition of a material  $M$  on a foreign substrate  $S$  is shifted negative from the equilibrium potential  $U_{eq}(M^+/M)$  for the  $M^+/M$  couple, often by as much as several hundred millivolts. This shift is often termed the nucleation (or critical) overpotential  $\eta_n(M^+/S)$ , and is defined as  $|U_n(M^+/S) - U_{eq}(M^+/M)|$  [1,2]. The observation of a nucleation overpotential ( $\eta_n(M^+/S) > 0$ ) is ubiquitous in electrodeposition by Volmer–Weber island growth.

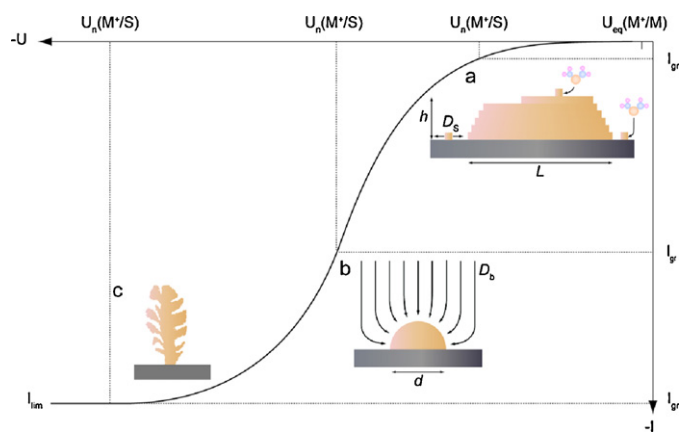
The magnitude of the nucleation overpotential for deposition of a material on a foreign substrate has important implications for island growth and the evolution of surface morphology. In this paper we address several key issues: (1) how the nucleation over-

potential determines whether it is possible to access the kinetic island growth regime, (2) the implications of the nucleation overpotential on island shape and orientation, and (3) the consequences of the coupling between the island density (applied potential) and the island size at coalescence (grain size). We then discuss the kinetics of island growth in terms of the contributions to vertical and lateral growth. Finally, we present examples of experimental methods to manipulate the nucleation overpotential and overcome some of the limitations imposed by the nucleation overpotential.

## 2. Nucleation overpotential

As described above, we define the nucleation overpotential  $\eta_n(M^+/S)$ , as the potential corresponding to the onset of deposition for the reaction  $M^+ + S + e^- \rightarrow M-S$  referenced to the equilibrium potential for the  $M^+/M$  couple. The onset potential is the potential at which material  $M$  is first detected on the substrate and hence is not a thermodynamic quantity. Furthermore, the onset potential may be dependent on surface area, the time scale of the experiment, and the atomic structure of the substrate. The onset potential can be measured by *in situ* methods such as quartz crystal microbalance measurements, scanning probe microscopy, chronoamperometry, or voltammetry, or by *ex situ* methods such as electron microscopy, scanning probe microscopy, or surface spectroscopy (e.g. X-ray photoelectron spectroscopy). Since electrochemical methods may be problematic due to the formation of intermediates or side reactions, direct observation of the formation of islands is usually preferable.

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**Fig. 1.** Steady state current–voltage curve for the deposition of material  $M$  on substrate  $S$ . The nucleation potential for deposition of material  $M$  on substrate  $S$  is indicated for (a) kinetic control, (b) mixed kinetic/diffusion control, and (c) diffusion control. (a) Island growth is kinetically controlled regime such that the island shape is dictated by the energy of the different facets. (b) Island growth is under mixed kinetic/diffusion control, usually resulting in the formation of hemispherical islands. (c) Island growth is under diffusion control resulting in the formation of diffusion limited aggregates or dendrites.

The nucleation overpotential sets a lower limit on the island growth rate and hence is critical in determining whether the kinetic island growth regime can be accessed. The three regimes of electrochemical growth are represented graphically in Fig. 1. The solid curve in the figure represents the deposition current for deposition of material  $M$  onto substrate  $M$ . After nucleation of material  $M$  on substrate  $S$ , the growth rate of islands is determined largely by the overpotential for deposition of  $M$  on  $M$ , i.e.  $U_{\text{appl}}(M^+/M) - U_{\text{eq}}(M^+/M)$ , where  $U_{\text{appl}}(M^+/M)$  is the applied (deposition) potential. Below we discuss these three regimes in electrochemical growth.

### 2.1. Small nucleation overpotential

For a system where  $U_n(M^+/S)$  is close to  $U_{\text{eq}}(M^+/M)$ , island growth after nucleation can be sufficiently slow so that growth is in the kinetic regime. Under these conditions, there are two contributions to island growth: direct attachment to the island ( $M^+ + e^- + M \rightarrow M_{\text{ads}}-M$ ) and indirect attachment resulting from adatom formation on the substrate ( $M^+ + e^- + S \rightarrow M_{\text{ads}}-S$ ) and subsequent surface diffusion. In general, direct attachment results in vertical growth whereas indirect attachment results in attachment of adatoms at the island perimeter and hence contributes to lateral growth.

The relative rates of deposition on the substrate  $S$  and island  $M$  can be described in terms of the probability [3,4] of electron transfer:  $P_{M-S}$  is the probability that a metal ion is reduced directly onto the substrate and  $P_{M-M}$  is the probability that a metal ion is reduced to a metal atom on a growing island. It is evident that Volmer–Weber island growth occurs when  $P_{M-S} < P_{M-M}$ . Macroscopically this is equivalent to the case where the rate of reduction onto the substrate is lower than the rate of reduction onto the same metal. The use of deposition probabilities is convenient since the equilibrium potential for a redox couple consisting of metal ions and a foreign metal substrate ( $M^+/S$ ) cannot be defined.

The formation of faceted islands requires slow direct attachment on the facets, i.e. layer-by-layer (or spiral) growth. Thus, we have the unusual situation with macroscopic Volmer–Weber island growth on the substrate, but layer-by-layer growth on the island facets. The kinetics of island growth is discussed in Section 3. As the potential becomes more negative, the flux to the islands increases and eventually reaches the point

where layer-by-layer growth can no longer be sustained on the facets.

### 2.2. Moderate nucleation overpotential $\eta_n(M^+/S)$

For a system where the onset of deposition is far from the equilibrium potential for the  $M^+/M$  couple, the deposition current, and hence the flux of metal ions to the growing islands, is very high. The high flux limits adatom diffusion on the islands and hence prevents the evolution of well-defined facets. Under these conditions, the deposition is often under mixed diffusion/kinetic control, and radial transport of metal ions in bulk solution usually results in the formation of hemispherical islands. This regime is of technological interest since it is the regime where thin film deposition of a material on a foreign substrate is usually performed due to the high deposition rates. The current associated with nucleation and diffusion limited growth of hemispherical islands has been treated by Scharifker and co-workers [5–10].

### 2.3. Large nucleation overpotential

When  $U_n(M^+/S)$  is in the regime where deposition of  $M$  is diffusion limited, island growth immediately after nucleation is very fast. In this case, growth instabilities can lead to preferential attachment of metal ions at protuberances resulting in the formation of unusual morphologies. In extreme cases, for example in the absence of a supporting electrolyte, deposition results in the formation of diffusion limited aggregates, dense branching morphologies, or dendrites.

### 2.4. Summary

As discussed above, the nucleation overpotential  $\eta_n(M^+/S)$  determines whether the kinetic regime of island growth is accessible or not. Thus the magnitude of the nucleation overpotential is critical for a wide range of processes. For example, island shape can only be controlled in the kinetic regime, i.e. when  $\eta_n(M^+/S)$  is small. These implications are discussed in the following two sections.

## 3. Implications of nucleation overpotential on island growth

In electrocrystallization, nucleation occurs on an electrode surface, and hence both island shape and island orientation are important degrees of freedom in determining properties of arrays of islands (e.g. for catalysts) or coalesced islands (e.g. for thin films). The ability to independently dictate island shape and orientation is an area that has not received significant attention, despite its scientific and technological importance.

### 3.1. Island shape

The evolution of surface morphology close to equilibrium has been widely studied in crystal growth from bulk solution [11–24], but has not been widely studied in electrocrystallization (i.e. non-epitaxial systems that exhibit a Volmer–Weber island growth mode). The shape of islands in electrocrystallization can be understood in terms of the differences in surface energy of different crystallographic planes [25,26]. In general, growth rates are faster on higher energy facets, leading to crystals that are defined by facets with lower surface energy and hence lower growth rates (see Fig. 2).

The low energy facets for most crystals, in the absence of specific adsorption, are the planes with the highest density of atoms. For the cubic Bravais lattices, these are usually the  $\{111\}$  planes. However, it is well understood that the surface energy of crystallographic planes can be tuned by the selective adsorption of a molecule or ion,

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